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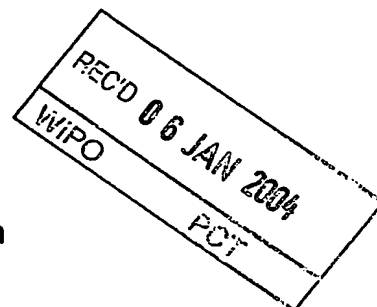
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Polymerization process

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### **POLYMERIZATION PROCESS**

The present invention relates to a process for the polymerisation of olefins and in particular to a process carried out in the gas phase in the presence of a supported catalyst system comprising a pretreated support material.

Processes for the co-polymerisation of olefins in the gas phase are well known in the art. Such processes can be conducted for example by introducing the gaseous monomer and comonomer into a stirred and/or gas fluidised bed comprising polyolefin and a catalyst for the polymerisation.

In the gas fluidised bed polymerisation of olefins, the polymerisation is conducted in a fluidised bed reactor wherein a bed of polymer particles is maintained in a fluidised state by means of an ascending gas stream comprising the gaseous reaction monomer. The start-up of such a polymerisation generally employs a bed of polymer particles similar to the polymer which it is desired to manufacture. During the course of polymerisation, fresh polymer is generated by the catalytic polymerisation of the monomer, and polymer product is withdrawn to maintain the bed at more or less constant volume. An industrially favoured process employs a fluidisation grid to distribute the fluidising gas to the bed, and to act as a support for the bed when the supply of gas is cut off. The polymer produced is generally withdrawn from the reactor via a discharge conduit arranged in the lower portion of the reactor, near the fluidisation grid. The fluidised bed consists in a bed of growing polymer particles. This bed is maintained in a fluidised condition by the continuous upward flow from the base of the reactor of a fluidising gas.

The polymerisation of olefins is an exothermic reaction and it is therefore

necessary to provide means to cool the bed to remove the heat of polymerisation. In the absence of such cooling the bed would increase in temperature and, for example, the catalyst becomes inactive or the bed commences to fuse. In the fluidised bed polymerisation of olefins, the preferred method for removing the heat of polymerisation is by supplying to the polymerisation reactor a gas, the fluidising gas, which is at a temperature lower than the desired polymerisation temperature, passing the gas through the fluidised bed to conduct away the heat of polymerisation, removing the gas from the reactor and cooling it by passage through an external heat exchanger, and recycling it to the bed. The temperature of the recycle gas can be adjusted in the heat exchanger to maintain the fluidised bed at the desired polymerisation temperature. In this method of polymerising alpha olefins, the recycle gas generally comprises the monomer and comonomer olefins, optionally together with, for example, an inert diluent gas such as nitrogen or a gaseous chain transfer agent such as hydrogen. Thus, the recycle gas serves to supply the monomer to the bed, to fluidise the bed, and to maintain the bed at the desired temperature. Monomers consumed by the polymerisation reaction are normally replaced by adding make up gas or liquid to the polymerisation zone or reaction loop.

It is also well known that fouling in gas phase polymerisation process can be a major problem, and can be caused by non-uniform fluidisation as well as poor heat transfer in the polymerisation process. Catalyst and polymer particles may adhere together or to the walls of the reactor and continue to polymerise, and often fuse together and form chunks, which can be detrimental to a continuous process, particularly a fluidised bed process

The incorporation of antistatic agents in polymerisation catalysts is well known. For example US 5414064 describes the use of Stadis with chromium based catalysts while US 5498581 describes again the use of Stadis with silica supported metallocene catalyst systems.

US 6469111 describes the gas phase polymerisation of olefins using a catalyst system containing an antistatic agent based on magnesium oxide or zinc oxide. The oxides are used in a mixture with a supported polymerisation catalyst component. The catalyst systems described therein include supported chromium oxide catalysts and also supported metallocene complexes in particular bis(cyclopentadienyl) metallocene

complexes.

More recently WO 02/066524 describes supported catalysts for olefin polymerisation comprising a combination of a sulfated metal oxide support and an aluminoxane.. The sulphated metal oxide support may be easily prepared by contacting  
5 a precursor metal oxide with a material having a  $\text{SO}_4$  group such as sulphuric acid or ammonium sulphate. Typically the resultant aluminoxane deposited on the sulphated metal oxide is used with an organometallic complex of a Group 4 metal, in particular with metallocene complexes comprising both a cyclopentadienyl ligand and a phosphinimine ligand. The catalyst systems reported therein exhibit improved activity.

10 We have now surprisingly found that the pretreatment of support materials with certain sulphate compounds leads to supported catalyst systems which when used for the gas phase (co-) polymerisation of olefins in a fluidised bed reactor leads to a reduction in static levels on the resultant polymers thereby reducing fouling.

Thus according to the present invention there is provided a process for reducing  
15 fouling during the gas phase (co-) polymerisation of olefins in a fluidised bed reactor comprising (co-) polymerising said olefins in the presence of a catalyst system comprising:

(a) a transition metal compound,

(b) an activator, and

20 (c) a catalyst support component

*characterised in that* the support component has been pretreated with an  $\text{SO}_4$  containing compound..

Suitable  $\text{SO}_4$  containing compounds include both metal and non-metal sulphates.

Preferred metal sulphates are transition metal sulphates for example sulphates of  
25 iron, copper, zinc, nickel and cobalt. Particularly preferred are sulphates of iron and copper.

Preferred non-metal sulphates are ammonium sulphates.

Sulphuric acid is also particularly suitable for use in the process of the present invention.

30 The support component may be an inorganic oxide, a clay or may be a polymeric support material.

The most preferred support material for use with the supported catalysts

according to the process of the present invention are inorganic oxides in particular oxides of aluminium, silicon, zirconium, zinc and titanium. Alumina, silica and silica-alumina are preferred metal oxides. Suitable silicas include Crosfield ES70, Davison 948 and Sylopol 948 silicas.

5       The support material is preferably treated with a water solution of the required inorganic metal salt.

      The support material may then be further subjected to a heat treatment and/or chemical treatment to reduce the water content or the hydroxyl content of the support material. Typically chemical dehydration agents are reactive metal hydrides, aluminium  
10   alkyls and halides. Prior to its use the support material may be subjected to treatment at 100°C to 1000°C and preferably at 200 to 850°C in an inert atmosphere under reduced pressure.

      The support material may be further combined with an organometallic compound preferably an organoaluminium compound and most preferably a  
15   trialkylaluminium compound in a dilute solvent.

      The support material is pretreated with the organometallic compound at a temperature of -20°C to 150°C and preferably at 20°C to 100°C.

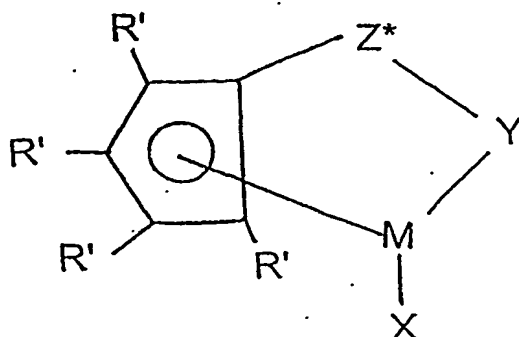
      The transition metal compound may be any suitable compound known in the art for use as a catalyst component for the polymerisation of olefins. For example  
20   traditional polymerisation catalysts based on chromium or titanium metals may be suitable.

      The preferred transition metal compounds are metallocene complexes.

      Typically the metallocene complex comprises a bis(cyclopentadienyl) zirconium complex for example bis(cyclopentadienyl) zirconium dichloride or  
25   bis(tetramethylcyclopentadienyl) zirconium dichloride. Examples of such complexes may be found in EP 129368, EP 206794, and EP 260130.

      Particularly preferred metallocene complexes are monocyclopentadienyl complexes. Such complexes have been referred to as 'constrained geometry' complexes and examples of these complexes may be found in EP 416815 or EP 420436.

30       The preferred monocyclopentadienyl metallocene complexes have the formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral  $\eta^4$  bonded diene group having up to 30 non-hydrogen atoms, which forms a  $\pi$  complex with M;

Y is -O-, -S-, -NR\*-, -PR\*-;

M is titanium or zirconium in the + 2 formal oxidation state;

Z\* is  $\text{SiR}^*_2$ ,  $\text{CR}^*_2$ ,  $\text{SiR}^*_2\text{SiR}^*_2$ ,  $\text{CR}^*_2\text{CR}^*_2$ ,  $\text{CR}^*=\text{CR}^*$ ,  $\text{CR}^*_2\text{SiR}^*_2$ , or  $\text{GeR}^*_2$ , wherein:

R\* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R\* having up to 10 non-hydrogen atoms, and optionally, two R\* groups from Z\* (when R\* is not hydrogen), or an R\* group from Z\* and an R\* group from Y form a ring system,

Examples of suitable X groups include s-trans- $\eta^4$ -1,4-diphenyl-1,3-butadiene, s-trans- $\eta^4$ -3-methyl-1,3-pentadiene; s-trans- $\eta^4$ -2,4-hexadiene; s-trans- $\eta^4$ -1,3-pentadiene; s-trans- $\eta^4$ -1,4-ditolyl-1,3-butadiene; s-trans- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene; s-cis- $\eta^4$ -3-methyl-1,3-pentadiene; s-cis- $\eta^4$ -1,4-dibenzyl-1,3-butadiene; s-cis-

$\eta^4$ -1,3-pentadiene; s-cis- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a  $\pi$ -complex as defined herein with the metal.

Most preferably R' is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or phenyl or 2 R' groups (except hydrogen) are linked together, the entire  
5 C<sub>5</sub>R'<sub>4</sub> group thereby being, for example, an indenyl, tetrahydroindenyl, fluorenyl, tetrahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosphorus containing groups containing a group corresponding to the formula -N(R'')- or -P(R'')- wherein R'' is C<sub>1-10</sub> hydrocarbyl.

10 Most preferred complexes are amidosilane - or amidoalkanediyl complexes.

Most preferred complexes are those wherein M is titanium.

Specific complexes suitable for use in the process according to the present invention are those disclosed in the aforementioned WO 95/00526, the relevant parts of which are incorporated herein by reference.

15 A particularly preferred complex for use in the present invention is (t-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl) dimethyl silanetitanium - $\eta^4$ -1,3-pentadiene.

The activator component may be chosen from a wide range of compounds well known in the art for the activation of transition metal compounds.

20 Aluminoxanes are well known as activators for metallocene complexes. Suitable aluminoxanes, for use in the process of the present invention, include polymeric or oligomeric aluminoxanes in particular methyl aluminoxane (MAO).

Another type of activator compounds are organoboron compounds.

Preferred organoboron compounds are triarylboron compounds, in particular  
25 perfluorinated triarylboron compounds.

The most preferred organoboron compound is tris(pentafluorophenyl) borane (FAB).

Preferred activators for use in the present invention are ionic compounds comprising a cation and an anion.

30 The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylium cations, oxonium cations, organometallic cations and cationic oxidizing agents.



Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

The preferred ionic activators used as activators are those wherein the cation of the ionic activator comprises a hydrocarbyl substituted ammonium salt and the anion comprises an aryl substituted borate.

Typical borates suitable as ionic activators include:

triethylammonium tetraphenylborate  
triethylammonium tetraphenylborate,  
10 tripropylammonium tetraphenylborate,  
tri(n-butyl)ammonium tetraphenylborate,  
tri(t-butyl)ammonium tetraphenylborate,  
N,N-dimethylanilinium tetraphenylborate,  
N,N-diethylanilinium tetraphenylborate,  
15 trimethylammonium tetrakis(pentafluorophenyl) borate,  
triethylammonium tetrakis(pentafluorophenyl) borate,  
tripropylammonium tetrakis(pentafluorophenyl) borate,  
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,  
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,  
20 N,N-diethylanilinium tetrakis(pentafluorophenyl) borate.

Particularly suitable activators of this type are those ionic activators comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen,

Suitable activators of this preferred type are described in WO 98/27119 the 25 relevant portions of which are incorporated herein by reference.

Most particularly preferred activators of this type are alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred activator is bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate.

30 The preferred gas phase process takes place continuously in a fluidised bed.

The continuous polymerisation is effected in the gas phase at elevated temperature in the presence of a fluidised bed of polymer particles and continuous

recycle of unreacted monomer(s) around a loop joining the inlet and outlet of the reactor containing the fluidised bed. Examples of two possible approaches are described in EP 89961, US 53527947 and US 5541270 the complete texts of which are herein incorporated by reference. EP 699213 also illustrates a possible approach and again the complete text of this publication is incorporated by reference.

The process of the present invention is suitable for the polymerisation of ethylene or the copolymerisation of ethylene with one or more alpha-olefins having from three to twenty carbon atoms. Preferably the alpha-olefin has between three and ten carbon atoms most preferably three and eight. Examples of the most preferred alpha olefins include 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene.

The process of the present invention is most particularly directed to the preparation of copolymers of ethylene with alpha-olefins having at least 6 carbon atoms in particular to copolymers of ethylene with 1-hexene or 4-methyl-1-pentene.

The present invention will now be further illustrated by reference to the following examples:

#### Abbreviations

TEA	triethylaluminium
Ionic Activator A	$[N(H)Me(C_{18-22}H_{37-45})_2][B(C_6F_5)_3(C_6H_4OH)]$
Complex A	$(C_5Me_4SiMe_2N^tBu)Ti(\eta^4-1,3-pentadiene)$

#### Example 1

##### Preparation of modified silicas

A sulphuric acid modified silica (A) was prepared as follows: to 25 g silica Sylopol 948 dispersed in 125 ml of water was added dropwise 7.06 g of sulphuric acid. The solvent was then removed by heating at 115°C overnight. The silica was then calcined under nitrogen at 250°C for 5h

For comparison, 20 g silica Sylopol was calcined under nitrogen at 250°C for 5 hours to give Silica B

##### Catalyst preparation

#### Example 2

To a suspension of 10 g of silica A (as described above) in hexane (50 ml) was added 7.4 ml of TEA (solution in hexane,  $[Al] = 1.027 \text{ mol/l}$ ) and 8.4 ml of TiBAI (solution in hexane,  $0.952 \text{ mol/l}$ ). The mixture was allowed to react for 30 minutes then

the liquid fraction was filtered and the remaining solid was washed with 3 x 20 ml of hexane and finally dried under vacuum.

$$[Al] = 1.35 \text{ mmol/g}$$

To 1.485 ml of a toluene solution (11.1 wt%) of Hiribs2 was added 0.252 ml of a toluene solution of TEA ( $[Al]=0.25 \text{ mol/l}$ ). This solution was then added to 4g of the above prepared silica/(TEA+TiBA) and the mixture was well agitated until non lumps were visible and was allowed to stand for 30 min. 0.705 ml of an heptane solution of CGC7 (9.17% wt) was then impregnated. The mixture was well agitated until non lumps were visible and was allowed to stand for 30 min

10.42 ml of hexane were then added then the liquid fraction was filtered and the remaining solid was washed with 3 x 20 ml of hexane and finally dried under vacuum.

$$[Al] = 1.28 \text{ mmol/g}$$

$$[Ti] = 31 \text{ } \mu\text{mol/g}$$

#### Example 3 (Comparative)

To a suspension of 5.404 g of silica B (as described above) in hexane (30 ml) was added 10 ml of TEA (solution in hexane,  $[Al] = 1.047 \text{ mol/l}$ ). The mixture was allowed to react for 30 minutes then the liquid fraction was filtered and the remaining solid was washed with 3 x 20 ml of hexane and finally dried under vacuum.

$$[Al] = 1.54 \text{ mmol/g}$$

To 1.485 ml of a toluene solution (11.1 wt%) of Hiribs2 was added 0.252 ml of a toluene solution of TEA ( $[Al]=0.25 \text{ mol/l}$ ). This solution was then added to 4g of the above prepared silica/TEA and the mixture was well agitated until non lumps were visible and was allowed to stand for 30 min. 0.705 ml of an heptane solution of CGC7 (9.17% wt) was then impregnated. The mixture was well agitated until non lumps were visible and was allowed to stand for 30 min

10.42 ml of hexane were then added then the liquid fraction was filtered and the remaining solid was washed with 3 x 20 ml of hexane and finally dried under vacuum.

$$[Al] = 1.43 \text{ mmol/g}$$

$$[Ti] = 37.5 \text{ } \mu\text{mol/g}$$

#### Polymerisation data

#### Gas Phase Polymerizations

The following gas phase polymerisations were carried using the above supported

catalyst compositions:

Run	Catalyst	Agitation speed	Ethylene	1- Hexene	Hydrogen	Catalyst	Time
		(rev/min)	(bar)	(ppm)	(ml)	(g)	(hrs)
1	Example 2	100	6.5	6500	50	0.098	1.17
2	Example 3 (Comparative)	100	6.5	6300	40	0.100	1

The activities and the product characteristics are shown below. Electrostatic charges was measured under same conditions using a Valitec Electrastatic sensor on the polyethylene powder when downloaded from the reactor.

Run <sup>o</sup>	Activity	Melt Index (2.16 kg)	Density	Electrostatic charge
	(g/mmol.h.bar)	g/10 min)	(g/ml)	(KV/inch)
1	1830	1.5	0.921	-0.4
2	2520	1	0.927	-2

Polymer made using a catalyst based on sulphuric acid modified silica clearly shows lower static charge than the reference example.

Claims:

1. A process for reducing fouling during the gas phase (co-) polymerisation of olefins in a fluidised bed reactor comprising (co-) polymerising said olefins in the presence of a catalyst system comprising:

- (a) a transition metal compound,
- (b) an activator, and
- (c) a catalyst support component

*characterised in that* the support component has been pretreated with an  $\text{SO}_4$  containing compound..

**ABSTRACT**  
**POLYMERIZATION PROCESS**

A process for reducing fouling during gas phase (co-) polymerisation of olefins in a fluidised bed reactor is performed in the presence of a catalyst system comprising:

(a) a transition metal compound,

(b) an activator, and

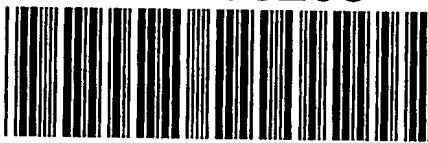
(c) a catalyst support component

wherein the support component has been pretreated with an  $\text{SO}_4$  containing compound.

A preferred compound is sulphuric acid and the supported catalyst systems preferably comprise a metallocene complex as the transition metal compound.

PCT Application

**GB0305208**



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